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**The mechanical properties of flax fibre reinforced poly (lactic acid) bio-composites  
to wet, freezing and humid environments**

Hossein Mohammad Khanlou<sup>a</sup>, Wayne Hall<sup>a</sup>, Peter Woodfield<sup>a</sup>, John Summerscales<sup>b</sup>, Gaston Francucci<sup>\*c</sup>

<sup>a</sup> Griffith School of Engineering, Gold Coast Campus, Griffith University, Queensland 4222, Australia

<sup>b</sup> Advanced Composites Manufacturing Centre, School of Engineering, Reynolds Building, University of Plymouth, Plymouth, Devon PL4 8AA, United Kingdom

<sup>c</sup> Research institute of materials science and technology (INTEMA-CONICET), National University of Mar del Plata, Mar del Plata B7600, Argentina.

\*Corresponding author: [gfrancucci@fi.mdp.edu.ar](mailto:gfrancucci@fi.mdp.edu.ar), +5492236022676.

**Abstract:** Bio-composites are increasingly being perceived as a green alternative to synthetic composites in many applications. However, the overall long-term durability of bio-composites is a major concern, particularly their ability for sustained performance under harsh and changing environmental conditions. This paper reports a detailed study on the effect of environmental conditions on the performance of flax/PLA bio-composites. Neat poly (lactic acid) PLA and bio-composite samples were exposed to environments similar to those found outdoors: wet, freezing and humid. Moisture absorption and physical changes of specimens were periodically examined. Flexural and tensile properties were evaluated periodically to determine the detrimental effect of each exposure condition on the mechanical performance of bio-composites. Direct contact with liquid water is the most deteriorating environment for bio-composites. A drying process can partially restore the mechanical performance of these materials. Bio-composites can survive reliably in warm humid environments and in those that could create freeze and thaw cycles for short-term outdoor applications. The mechanisms and reasons involved in the degradation of the properties of green composites are discussed.

**Keywords:** natural fibres reinforced polymer composites; flax fibre; PLA; environmental application

#### **Abbreviations**

as-manufactured (AM)	natural fibre reinforced polymer (NFRP)
carbon fibre (CF)	Polylactic acid (PLA)
fibre reinforced polymer (FRP)	relative humidity (RH)
flax fibres (FF)	unidirectional (UD)
freeze/thaw (F/T)	water absorption (WA)
glass fibre (GF)	water saturated (WS)
humid saturated (HS)	water saturated and freeze/thaw (WSF/T)
life cycle analysis (LCA)	water saturated and completely dried (WSD)
moisture content (MC)	

## 1. INTRODUCTION

There is significant global interest in bio-composites due to their practical and potential environmental benefits. Bio-composites are commonly referred to as “sustainable composites”, but such claims are rarely supported by a full four pillars (economic, environmental, equity, governance) life cycle analysis (LCA)<sup>1</sup>. The attractive features of bio-composites are acceptable mechanical properties (which are now comparable to unsustainable alternatives), reasonable price, low density, bio-compatibility and, subject to LCA, good sustainability<sup>1</sup>. These points encourage manufacturing industries (especially packaging and automotive<sup>2</sup>) to produce sustainable products using bio-composites. However, low durability and swift degradation of bio-composites in outdoor applications has become a chief obstacle. In particular, wet environments can cause a rapid deterioration of mechanical properties and performance of bio-composites due to moisture absorption<sup>3</sup> and dimensional changes<sup>4</sup>. Knowledge of the sensitivity of properties of bio-composites to moist environments is essential for prospective applications.

Water immersion, humidity and freeze/thaw (F/T) tests are the main tools in recognizing the sensitivity of bio-composites to the environment<sup>5-8</sup>. The quality of the bio-composite can be explained by using a range of environments, from a fully wet environment to an environment where the water absorption level changes due to freezing and thawing (F/T). Table 1 shows that all three types of moisture-related environments can cause major degradation in mechanical properties. Although several studies regarding the degradation of NFRP bio-composites have been published (Table 1), there is a need for further studies to generate a complete understanding of bio-composites in various environments for various applications. When the durability in specific environments is determined, practitioners may be able to accordingly adjust their plans for the usage of the bio-composite.

Moisture can cause both physical and chemical degradation of bio-composites. Physical changes were introduced by previous studies<sup>9-13</sup> as a key factor in bio-composites durability reduction. The source of physical changes is the swelling of the hydrophilic fibres which cause micro-cracks in the bio-composite<sup>10, 14</sup>. Then, capillary action transports water along the bio-composite layers<sup>10, 14</sup>. Consequently, fibre and matrix debonding causes a decline in the mechanical properties<sup>15, 16</sup>. Chemical degradation reactions involve water molecules

interacting with hydroxyl and carboxyl groups found in cellulose, hemicellulose and lignin which are the principal components of natural fibres<sup>14</sup>. These reactions cause reductions in the molar mass of the natural polymers and degradation of the bonding between fibre and matrix leading to further degradation of mechanical properties.

In this work, the sensitivity of the compression moulded flax fibre (FF)/PLA bio-composite, is examined in water saturated (WS), humid saturated (HS) and F/T environments, and the tensile and flexural properties of the bio-composite are reported, resulting in a comprehensive set of experimental data and the related kinetic data. The findings are also compared with those of previous works which have been produced for various applications. As characteristics of WSD, F/T, WSF/T bio-composites are rarely discussed in the literature, the discussion of this study is valuable for practitioners who are considering using FF/bio-matrix products.

## **2. EXPERIMENTAL PROCEDURE**

### **2.1 Materials**

Unidirectional (UD) flaxply fabric (180 g/m<sup>2</sup> flax) manufactured by the Lineo Company (France) was used in this study. PLA film (25 microns thick) was supplied by Magical Film Enterprises Co. Ltd. (Taiwan). Thermal transition temperatures of the PLA were measured for four samples using differential scanning calorimetry (DSC). The average glass transition temperature ( $T_g$ ) was 61.9 °C and the crystalline melting temperature ( $T_m$ ) was 146.2 °C.

### **2.2 Composites samples preparation**

Flat aluminium plates (3 mm thick) were treated with a high-temperature release agent (Aliphatic Hydrocarbones, Marbocote Ltd, UK), and used as the lower and upper moulding surface. Two layers of PLA film were placed directly on the bottom mould surface followed by a single layer of fibre and two further layers of PLA. This pattern was repeated for ten fabric layers. There are totally 10 layers of FF between each reinforcement layer. The as-manufactured (AM) unidirectional (UD) bio-composite plate was moulded with a total thickness of approximately 2.5 mm, with a planar area of approximately 300 × 300 mm to a nominal fibre volume fraction of 48%.

The compression moulding machine (Carver Inc, Wabash, USA) was set to a temperature of 170 °C which is above the melting temperature of the PLA. The composite was compressed to a pressure of 300 kPa and held at the set temperature for 15 minutes consolidation time. The pressure was maintained while the top and bottom platens were cooled. The cooling process was manually controlled by a supply of cold water to the platens. To accurately repeat the cooling process, the temperatures of the upper and lower platens were recorded during the entire process using a data logger (USB TC-08, Pico Tech, UK) sampling at a rate of 1 Hz.

The samples were cut by means of a laser cutter to the dimensions required for mechanical tests (tensile and flexural) and their edges were carefully coated with adhesive tape. A total five samples were tested for each condition.

### 2.3 Water immersion tests

Test samples were immersed in distilled water at room temperature. The samples were weighed periodically using an analytical scale accurate to 100 µg and the time of each weight measure was controlled with a chronometer. Before the weight measurements, the specimens were withdrawn from the water and wiped dry to remove the surface moisture. Then, the specimen weight and immersion time data were collected. The relative water absorption (WA) was calculated using Eq.(1):

$$M_r(t) = \frac{[W(t) - W_0]}{W_0} \times 100 \quad (1)$$

where  $M_r(t)$  = relative WA of the specimen at each time (t),  $W(t)$  = specimen weight at each time,  $W_0$  = initial specimen weight. The tests were stopped after 60 days.

One set of the WS samples were completely dried (WSD) to evaluate the residual properties of samples that have been fully saturated but then dried. The drying process was carried out in a dehydrating oven at 40 °C for three days (until no changes in the samples weight were observed). This drying cycle (low temperature-long time) was chosen to avoid possible damage to the mechanical properties of the bio-composite at higher temperatures.

### 2.4 Humidity tests

To perform the humidity test, specimens from each batch of tensile and flexural samples were put into an environmental test chamber with a relative humidity (RH) of 75% at 45 °C. During the ageing experiment, and at certain periods of time, specimens were periodically taken out of the chamber to assess the weight change. The weighing of the specimens was stopped after 60 days, when the weight reached saturation point, that is to say when the weight gain was nearly constant.

## **2.5 Freeze/Thaw tests**

Two types of F/T tests were designed: For first type, F/T cycling, at 1, 5 and 10 cycles, were performed on AM specimens following the ASTM D7031-04 standard recommendations. Each cycle consisted of placing the specimens in a freezer for a 24 h freezing period at -18 °C and removing them from the freezer to allow thawing at room temperature for another 24 hours. For second type, the WS samples were subjected to 1, 5 and 10 cycles of F/T; for a 24 h thawing period, the samples were kept in the water to ensure the water content remained at the saturation level. This type of test shows the mechanical performance of the materials under freezing process at the most favorable condition (AM samples) and the most unfavorable condition (maximum moisture content (MC) in the microstructure).

## **2.6 Mechanical properties evaluation**

Test specimens were laser cut from the composite plates (parallel to the fibre direction). The test specimen dimensions were 250 mm × 15 mm and 80 mm × 12.7 mm for the tensile and flexural tests, respectively. Four samples were tested for each condition. Tensile testing was carried out using an Instron 3367 testing machine with an Instron 30 kN load cell (serial no. 68296). Gripping end tabs were used during the tensile testing as recommended by ASTM D3039/D3039 M. Crosshead displacement rate was 2mm/min. The tensile strain in the specimens was measured with a 50 mm Instron extensometer attached to the in-plane surface of the sample. The tensile modulus was calculated over the axial strain range of 1000-3000 micro strain.

Three point bending tests were performed with the same testing machine, a test span of 60 mm and a crosshead displacement rate of 2.4 mm/min. Load-displacement curves were

obtained from these tests and flexural modulus and strength values were determined from these curves, according to the ASTM D790-03 standard.

### 3. RESULTS AND INTERPRETATION

#### 3.1 Moisture absorption and physical changes

When a solid material is immersed in water, or exposed to a very humid environment a diffusion process takes place due to the water concentration gradient between the solid and the surroundings. If the water transport from one part of the system to another is carried out by means of random molecular motion driven by this concentration gradient, then Fick's first law (Eq. (2)) is applicable:

$$F = -D \frac{\partial C}{\partial x} \quad (2)$$

where  $F$  is the rate of transfer in the  $x$  direction per unit area of a section,  $C$  is the concentration of the diffusion substance,  $x$  is the space coordinate measured normal to the section, and  $D$  is the diffusion coefficient of the solid.

In the case of composite materials and specially in vegetable fibre composites, there are some additional water transport mechanisms apart from the diffusive ones, such as: movement of water molecules into voids and defects at the fibre/matrix interface as a result of capillary action<sup>9, 14</sup>, and capillary flow into micro-cracks in the matrix after swelling of natural fibres<sup>10</sup>. Therefore, Fick's law assumptions are not accomplished in these materials. Several models have been developed to calculate the diffusion of molecules within a composite, however Fick's second law (Eq. (3)) has still been widely used to estimate a one dimensional time dependent WA process<sup>19</sup>.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3)$$

In this case, if the diffusion coefficient is considered to be constant, the concentration gradient is only along the  $x$ -axis and diffusion is one dimensional, then the fundamental differential equation of diffusion in an isotropic medium (and again, the composite is considered to be isotropic) is derived by considering a rectangle whose sides are parallel to



the coordinate axes<sup>19</sup>. Thus, for a plane sheet with uniform initial distribution and a constant surface concentration, the moisture uptake with respect to exposure time can be calculated using Eq. (4)<sup>19</sup>:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{(4l^2)}\right] \quad (4)$$

where  $M_t$  is the total mass of diffusion substance entering the sheet at time  $t$ ,  $M_\infty$  is the corresponding quantity after infinite time, and  $l$  is the half thickness of the specimen. Eq. (4) demonstrates that  $M_t$  equals  $M_\infty$  at infinite time, and infinite time is typically considered when MC is at the maximum level. The plateau section at the last stage of WA in Fig. 1 shows the maximum level of MC or  $M_\infty$ . Furthermore, MC at the initial stage rises linearly with  $t^{0.5}$  and can be simplified as Eq. (4) to Eq. (5)<sup>19</sup>:

$$M_t = \frac{2M_\infty \sqrt{D}}{\sqrt{\pi}} \frac{\sqrt{t}}{l} \quad (5)$$

Therefore,  $D_{average}$  or average of diffusion coefficient can be estimated by using Eq. (6)<sup>19</sup>:

$$D_{average} = \frac{\pi}{4} M_\infty^{-2} l^2 \theta^2 \quad (6)$$

where  $\theta$  is the slope of  $M_t$  against  $t^{0.5}$  plot.

However, these assumptions are again not realistic since the composite material is not isotropic, and the diffusion coefficient is unlikely to remain constant as the different transport mechanisms previously mentioned activates or arrests as the water absorption process takes place. The development of a realistic model accounting for all the phenomena occurring during water diffusion through vegetable fibre reinforced composites is beyond this work objective. Therefore, in order to obtain numerical values giving a tangible comparison of the diffusion characteristics of the bio-composites used in this study exposed to the different environments, Fick's law was still used, and diffusion was evaluated by MC% measurements, and by considering the slope of the first part of MC against  $t^{0.5}$ . The calculated diffusion coefficient was then called "effective" diffusion coefficient, since it involves not only diffusive mechanisms for water transport through the material, but the others previously mentioned.

Fig. 1a represents MC percentage as a function of time (NB: days on the time axis) for PLA and the FF/PLA bio-composite in the different environments, including WS, HS and F/T. Following Fick's diffusion theory, the relative MC in the immersion process should display three stages, a linear rise against  $t^{0.5}$  at the beginning, then the absorption rate decreases, and finally a (quasi-)steady saturated stage is reached. This behaviour was only observed for the water immersed samples bio-composites, although the behaviour is not perfectly Fickian. As can be seen in Fig. 1a, MC at HS environment is significantly lower than WS environment. While MC is very low, it has three clear stages. This stepped process can be attributed to swelling stresses that arise as the fibres confined inside the matrix absorb water and swell, and was previously observed and reported by Stamboulis et al.<sup>11</sup>. This mechanism slows down the approach to the final equilibrium moisture and a first apparent equilibrium occurs. After the initial absorption process, these stresses relax<sup>20</sup>, and the equilibrium moisture condition changes as the diffusion proceeds. A new equilibrium is reached and the process can continue or stop, if the saturation moisture content in the material is attained. The bio-composites showed three equilibriums, being the last one reached after 20 days and showing a  $\approx 2.5\%$  MC. No further equilibriums were observed from that point up to the tests final, 40 days after, thus it can be certainly stated that  $\approx 2.5\%$  was the saturation moisture content in these materials under the HS condition.

Although it was anticipated that there would not be MC in the bio-composite after the F/T process, some weight increase was registered, meaning that WA did occur. The WA occurs probably because of the swelling/shrinkage tensions encountered by the bio-composite during the F/T process. Moreover, when the bio-composite is transformed from the freeze phase to the thaw phase, the moisture from the environment condenses on the cold composite surface. This condition simulates dew and rainfall, and results in both cyclic washing away of the specimen surface and water absorption through the material. MC of water saturated and freeze/thaw (WSF/T) at 1, 5 and 10 cycles were approximately 22%, showing that the MC does not change after the WSF/T condition.

MC of neat PLA in WS gradually increases and levels off at 0.99% after 42 days, which is in agreement with  $MC \approx 1\%$  as reported by Wang et al.<sup>21</sup>. However, in the case of HDPE, it is reported that no moisture was gained after one year<sup>19</sup>. The very low MC in the matrix

suggests that water penetrates through the fibres in the composite, which function like water channels <sup>22</sup>.

Fig. 1b shows the same data as Fig. 1a except that the vertical axis has been normalized to the saturation moisture uptake,  $M_{\infty}$ . Table 2 shows the effective diffusion coefficients obtained by fitting Eq. (5) to the initial slope data against  $t^{0.5}$  from each of the experiments. Eqs. (4) and (5) are plotted on Fig. 1b for the cases of immersion and humid environments. Modelling of immersion and humidity tests show that the WA follows the initial stage of Fick's law up to  $M_t/M_{\infty} = 0.6$ . Data beyond this point were not used to estimate the initial slope for the effective diffusion coefficient. Therefore, it should be noted that only the first linear part of the HS specimens curve was used, and the effective effective diffusion coefficient represents the initial diffusion characteristics of the bio-composites.

To evaluate the physical changes of the bio-composite in different environments, the thickness of swollen material was calculated using Eq. (7):

$$f_{swelling(t)} = 100 \times \frac{T_{f,t} - T_{f,0}}{T_{f,0}} \quad (7)$$

where  $f_{swelling(t)}$  is the thickness swelling ratio,  $T_{f,t}$  is the bio-composite thickness exposed to the environment, and  $T_{f,0}$  is the AM bio-composite thickness.

Fig. 2 represents the physical changes of the bio-composite in different environments over time. The swelling of the WS bio-composite is significantly higher than the swelling in other environments, displaying the same trend as the MC. As mentioned before, the chemical composition of FF is responsible for the composite physical changes and this phenomenon can clearly be shown by the value of  $f_{swelling-PLA}$  in Fig. 2, which is only 0.13% in comparison with 19.5% for the bio-composite. Moreover, the HS environment does not impact on the physical changes of the bio-composite in a significant way. The negligible swelling changes can be of interest to practitioners who want to use the bio-composite in a HS environment. In addition to that, F/T leads to limited swelling in the thickness of bio-composite over the entire cycling period. Furthermore,  $f_{swelling}$  values of WSF/T at 1, 5 and 10 cycles were approximately 20%, 24% and 29%, showing significant F/T effects on the swelling of WS bio-

composites after F/T cycling. As it was expected, these swelling values significantly affected the mechanical properties (explained in the following sections).

Physical and chemical reactions, which cause the degradation process, occur in bio-composites. With the use of microscopes, initial defects have been seen to appear in the form of pores, micro-cracks and delamination<sup>13</sup>. These defects assist water permeating into the bio-composites by means of capillary transport, resulting in volumetric changes or swelling. Furthermore, hydrolytic reaction and the existence of H<sub>2</sub>O, causes chemical chain reactions in –CHCH<sub>3</sub>COO– groups of PLA molecules, which eventuate in the chain scission process and a decline in the molar mass and mechanical properties of the bio-composites<sup>13</sup>. All these reactions lead to interfacial and internal (centralized) degradations in the bio-composites. The following sections support this explanation.

### **3.2 Tensile properties**

Typical stress-strain curves for the FF/PLA composite at the different environments are shown in Fig. 3. For the immersion case and humid environment case, the examples shown in Fig. 3 correspond to 60 days of exposure to moisture-related environments. The bio-composite shows strain to failures of 2.3 to 3.4% for the WSD, F/T and HS samples, while WS and WSF/T samples show 3.8 to 4.3%. Generally, aging processes cause declines in stress and increases in strain, especially in the wet environments, in contrast to AM samples.

Fig. 4a-c shows the tensile properties (modulus, strength and strain at break) of the bio-composite exposed to various environments. Consistent with Fig. 3, exposure to moisture causes a decrease in tensile strength and an increase in failure strain. The elastic modulus determined by the initial slope of the stress/strain curves in Fig. 3 is most significantly affected by the immersion tests.

The tensile properties (modulus and strength) of the bio-composites show significant reductions after WS environment. These properties unexpectedly are restored after a complete drying process (compare WS and WSD in Fig. 3 and in Fig. 4). This finding highlights the importance of the drying process for regaining the properties, and shows the opportunity of using the bio-composites after simply drying them. This would be interest to the prospective bio-composite customers.

The HS environment also causes decreases (25%) in the tensile strength, but not as significantly as in the wet environment. One to ten cycles of F/T have a small negative impact on the tensile modulus. The mean tensile strengths are fairly consistent. However, 10 F/T cycling shows 29 and 23% decline in tensile modulus and strength, respectively, possibly due to the residual 1.5% MC of the sample. The tensile modulus and strength of the WSF/T bio-composite are as low as WS samples or even have some further degradation. This agrees with the fact that wet environment is the most deteriorating environment for bio-composites, even more than F/T environment.

The fracture strain almost doubles after WS. This can be explained by the WA plasticizing the NFRP bio-composites, as reported by Stamboulis et al.<sup>11</sup>, thus leading to increases in the maximum strain of the bio-composites. The strain-to-failure of the bio-composites after F/T-1 cycle is fairly similar to AM samples, and positively and gradually increases over the periods of F/T and WSF/T.

### **3.3 Flexural properties**

Flexural properties of FF/PLA bio-composites are shown in Fig. 5a-b. Flexural modulus and strength values of WS samples drop by 69% and 76% and the values are restored to only fall by 20% and 22% respectively, after the drying process. The HS environment also negatively affects flexural modulus and strength values by 39% and 24%, respectively. Flexural properties are not significantly influenced by the F/T process. However, the properties of WSF/T samples show similar behaviours to those of WS.

The reduction in flexural property after WA can be attributed to the weak FF/PLA interface in which moisture travels after WA. The micro-cracks on the surface of the bio-composite, which result from exposure to the environments, constrained the efficiency of stress transfer from PLA (matrix) to FF, leading to poor flexural properties<sup>23</sup>.

By comparing Fig. 4 and Fig. 5, it can be concluded that the trends of degradations in tensile and flexural properties are quite similar after exposure to the environments.

### **3.4 Effect of exposure time and moisture concentration on degradation**

Fig. 6 shows the deterioration of mechanical properties of the bio-composites which have similar deterioration trends over the process of WA, as the MC increased from initial point (AM specimens) to the saturation point (WS specimens).

Therefore, all above mentioned factors have constrained the NFRP bio-composite application for underwater usages. However, indoor applications or short outdoor applications can be considered for this kind of sustainable composites.

### 3.5 Visual observation of failures

Fig. 7 shows the fracture images from the edge of the bio-composites after exposure to different environments. Generally, cracks, fibre fracture, matrix cracking, fibre pull out and fibre debonding occur after an aging process, resulting in the sensitivity of bio-composites to different environments<sup>9, 24, 25</sup>. Fig. 7b-f show the moisture-exposed bio-composite layers have split after tensile failure. This phenomenon shows how interfacial surfaces between flax mat and PLA film layers are degraded over the aging processes, which are attributed to FF and PLA degradations during WA processes<sup>26, 27</sup>. This degradation can be easily identified from the colour changes of the WS, WSD and WSF/T samples. The HS samples have an insignificant WA, but do show these splitting layers as well as fibre breakage. It can also be argued that debonding of cells, monomers and the chain scission process of FF and PLA trigger this kind of degradation at 45 °C temperature<sup>27-31</sup>.

In addition, physical changes play an important role in the composite failures after environmental exposure. Newman et al.<sup>32, 33</sup> stated that the swelling of fibres causes stress in the surrounding matrix, as schematised in Fig. 8a (highlighted in hatched section). Some stresses are relieved in the matrix after relaxation (Fig. 8b). After the composite has dried, the matrix will not contract to the previous size due to distortion by molecular relaxation; although fibres do shrink on drying (Fig. 8c). This gap may be present in single fibre cells or in a bundle of cells (technical fibres)<sup>32</sup>. Gassan et al.<sup>34</sup> also reported the same problem using optical microscopy for plain-weave jute fibre reinforced epoxy composites. Newman et al.<sup>33</sup> and Homkhiew et al.<sup>23</sup> have also stated that cracks within a technical fibre may have appeared due to other damage mechanisms like cell-cell debonding. Thus, the effects of physical changes on the failure of bio-composites are undeniable.

As the swelling of PLA shows low sensitivity to WA, bio-composite swelling is significantly caused by fibre swelling. PLA exposed to HS and F/T environment shows the physical deterioration because of changes occurring at +45°C or -18°C temperatures. Random shattering of PLA at high or negative temperature has been suggested by Karlsson and Ndazi<sup>35</sup> to be the reason of deterioration; this suggestion can be seen in Fig.7e-f.

#### **4. Discussion**

As the findings of this study lead to several key points on the moisture-related environmental behaviours of bio-composites, this section focuses on the effect of moisture, redrying and freeze and thaw.

##### **4.1 Degradation due to the presence of moisture**

Several publications report the effect of moisture on mechanical properties of green composites and the findings here agree<sup>4, 10, 14, 26</sup>. In particular, compared with other environments, wet environments show the most severe deterioration of mechanical properties of bio-composites (for both tensile and flexural properties)<sup>9</sup>. To understand the mechanisms involved in the degradation of the properties of green composites, much consideration has been given to how water interacts with the composite [31-33].

Two types of water are defined to exist in the WS bio-composites<sup>15, 36</sup>. First, free water is defined as water molecules which are relatively free to travel through the free volume, micro voids and pores, while bound water is defined as that dispersed within the polymer matrix or attached to the polar groups of the polymer<sup>15, 36, 37</sup>. Both free water and bound water may exist in moisture absorbed by NFRP bio-composites. It would be interesting, but outside the scope of this study, to use nuclear magnetic resonance spectroscopy and (micro-)computed tomography (magnetic resonance imaging (MRI)) to follow the interactions of the two forms of water during diffusion<sup>38</sup>.

Moisture diffusion, and the consequent WA, in polymer composites is directed and controlled by various mechanisms:

- i. diffusion of water molecules into the free volume between the polymer molecular chains<sup>9</sup> and consequent plasticisation of the matrix,

- ii. diffusion of water molecules into the structure of fibres (resulting in hydrogen bonding with hydroxyl group of cellulose molecules) <sup>14</sup>,
- iii. movement of water molecules into voids and defects at the fibre/matrix interface as a result of capillary action <sup>9, 14</sup>, and
- iv. capillary flow into micro-cracks in the matrix after swelling of fibres <sup>10</sup>.

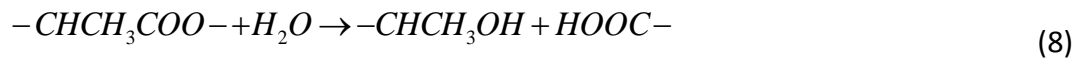
The hydrophilic nature of FF in which many hydroxyl groups (-OH) form numerous hydrogen bonds between the macromolecules of the cellulose and polymer, cause poor interfacial bonding between FF and PLA, leading to mechanical properties deterioration <sup>11, 26</sup>. MC of the bio-composite, which increases by means of capillary transport of FF, can negatively impact the FF/PLA interface and lead to delamination of the composites (see Fig. 7). These effects can be identified after the tensile fracture of the bio-composite (see Fig. 6).

To explain the role of fibre's structure, amorphous hemicelluloses (plant cell wall material associated with cellulose) and lignin are largely responsible for WA in plant fibres <sup>36, 39</sup> because they have higher free volume than the crystalline cellulose and hence facilitate easier water transport and access to hydrophilic groups. Since hemicelluloses constitute 16.7% of FF<sup>40</sup>, this can result in greater WA and then swift bio-degradation in plant fibres <sup>36, 39, 41</sup>.

The changes to the material due to moisture directly correspond to a decline in mechanical properties. Based on Figs 4 and 5, tensile properties are less sensitive to HS condition than flexural properties. Compared with full immersion all degradation mechanisms that occur in wet environments also take place in HS samples but with lower intensity. This can be observed by comparing the cases of AM, WS and HS in Figs 4 and 5. Mechanical properties of bio-composites are sensitive to a high temperature and it can accelerate the degradation process of bio-composites<sup>28</sup>. Dhakal et al. <sup>9</sup> examined the mechanical properties of hemp/unsaturated polyester composites in water at various temperatures they concluded that MC at 100°C reaches to equilibrium very fast compared to the samples immersed at lower temperatures; and consequently the composites significantly degraded due to crack development in the composites and loss of matrix at high accelerated aging process. Hu et al.<sup>13</sup> also reported that the tensile strength of jute/PLA appeared to decrease (~75%) after five days exposure at a hygrothermal environment, at 70°C.



The presence of moisture also leads to chemical degradation of the matrix and fibre of the bio-composite. Although the hydrolysis process is very slow at 45 °C for PLA, it can produce PLA degradation by breaking PLA molecular chains. The hydrolytic reaction (Eq. (8)) also occurs when  $-CHCH_3COO-$  groups on PLA molecules react with  $H_2O$  and form low molecular weight bio-composites<sup>13, 42</sup>:



Based on Figs 4 and 5, 25% and 24% reduction in tensile strength and flexural strength, respectively, occur after 60 days. These levels may be acceptable for users who are planning to use cheap and green composites for very short term applications in humid environments.

#### 4.2 Redrying of wet bio-composites

It has been reported by Baley et al.<sup>25</sup> that drying of natural fibres prior to composite manufacturing is not beneficial to tensile properties of bio-composites since it causes fibre shear and fibre peeling damages. However, the circumstances are different here in that the composite has already been manufactured and the level of water saturation is high.

As shown by comparing WS and WSD environments in Fig. 3, mechanical properties which are significantly influenced by an extremely wet environment, can be greatly restored by using an additional drying process. The practical implication is that if a bio-composite for short-term outdoor applications becomes wet, then simply allowing it to dry before reuse is a good strategy, especially when tensile properties/functions of the bio-composite are important.

#### 4.3 Degradation mechanism in F/T environment

In the literature, the effect of F/T environment has been only studied regarding the unsustainable composites, carbon fibre (CF) or glass fibre (GF) reinforced polymer composites (e.g.<sup>43-46</sup>). Belarbi et al.<sup>43</sup> reported insignificant effects of F/T condition on shear, axial and flexural properties of CF or GF reinforced polymer composites. However, the unsustainable composites become more brittle and fail catastrophically after the F/T cycling process<sup>44, 45</sup>. Cormier et al.<sup>46</sup> also provided a literature review on CF/epoxy and GF/epoxy composites with various constituents and processes used to manufacture composites, and concluded that F/T condition has a small negative effect on these composites.

In this study, the findings identified that F/T cycling has small negative impacts on mechanical properties of bio-composites. Tensile strength and flexural strength shows degradation as F/T cycling numbers increase, as samples are inclined to absorb moisture by which degradation happens. Bio-composite F/T cycling may produce internal stresses which cause micro-cracks, resulting in loss of tensile and flexural properties. In other words, moisture present in the fabrics prior to the manufacturing process, plus the moisture that was absorbed after every F/T cycle, suffered cycles of ice/water transformations, generating volume changes inside the materials microstructure, and thus internal stresses.

Bio-composites deteriorate significantly after WSF/T cycling. In this case, bio-composites contain substantial water in their microstructure which solidifies and melts in every F/T cycle. Therefore, these degradation mechanisms happen simultaneously with the ones caused by water immersion, leading to significant physical and chemical degradation, which are identifiable in both quantitative findings and image observations. In addition to similar damages from WS condition, WSF/T samples show significant physical and chemical degradation, which are identifiable in the results (cf. Figs 4 and 5).

## **5. Conclusion**

The sensitivity of properties of FF/PLA bio-composites to different environments was studied. Composites were exposed to the following conditions: water immersion, warm humid and F/T cycling environments. The mechanical performance (tensile and flexural properties), MC and physical changes (dimensional stability) of the composites during the exposure to the different environments were analyzed.

When FF/PLA composites are immersed in water, WA followed Fick's law. Tensile and flexural modulus and strength decreased significantly due to the quantity of water absorbed by the composites, which led to the development of different degradation mechanisms, such as the weakening of the FF/PLA interface and plasticisation. However, the tensile strain value found for the saturated specimens almost doubled that of "as manufactured" specimens due to the plasticising effect of water in FF/PLA bio-composites. Physical changes are relatively large, as the thickness of the samples increased considerably during the test.

After the saturation MC was reached in the immersion tests, some samples were completely dried to analyse the residual properties of the composites. The drying process proved to be effective in partially restoring the mechanical properties. However, the “as manufactured” properties were not reached, inferring that some permanent damage was caused after the immersion tests, which is most likely to be at the fibre-matrix interface. Nevertheless, it is advantageous to completely dry bio-composite prior to their structural application if they have high water content.

When exposed to a warm humid environment, both WA and physical changes were much lower than for water immersion, leading to lesser reductions in mechanical properties. In addition, hydrolysis process can be involved in the PLA degradation, decreasing the properties of the matrix and degrading the interfacial bonding between FF and PLA by molar mass degradation.

Freeze and thaw cycling has small negative impacts on tensile and flexural properties owing to small WA and physical changes, causing internal stresses.

Freeze and thaw cycling of WS specimens shows further deterioration of properties in comparison with the WS only specimens. WSF/T cycling damages the material because of the negative synergy caused by water trapped in the microstructure and freeze/thaw cycles, which leads to the development of internal stresses.

Altogether, based on the measurements and analyses, direct contact with liquid water is the most deteriorating environment for bio-composites and therefore underwater applications of these materials are strongly discouraged. In such cases, a drying process can restore partially the mechanical performance of these materials. On the other hand, bio-composites can endure reliably in warm humid environments and in those that could create F/T cycles for short-term outdoor applications.

### **Recommendations for future works:**

With the intention to estimate the consequent effects on the performance of composite parts, and its importance, there should be more investigations of the moisture absorption and swelling behaviour of NFRP composites. Conducting studies related to these conditions could lead to an insight into the degradation progress of NFRP bio-composites at moist environments.

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#### Figure Captions

Fig. 1.a) Moisture content (MC) and b)  $M_t/M_\infty$  rates of water saturated (WS) PLA and Flax/PLA bio-composites at WS, humid saturated (HS) and freeze/thaw (F/T) environments.

Fig. 2.a) Swelling rate of water saturated (WS) PLA and Flax/PLA bio-composites at WS, humid saturated (HS) and freeze/thaw (F/T) environments; b) magnified swelling rate of WS PLA, bio-composites at HS and F/T environments.

Fig. 3. Typical Flax/PLA bio-composites stress-strain curves at as-manufactured (AM), water saturated (WS), water saturated and completely dried (WSD), humid saturated (HS), freeze/thaw (F/T) and water saturated and freeze/thaw (WSF/T) environments.

Fig. 4. Tensile properties of the Flax/PLA bio-composite at as-manufactured (AM), water saturated (WS), water saturated and completely dried (WSD), humid saturated (HS), freeze/thaw (F/T) and water saturated and freeze/thaw (WSF/T) environments: (a) Modulus; (b) Tensile strength; and (c) Failure strain.

Fig. 5. Flexural properties of the Flax/PLA bio-composite at as-manufactured (AM), water saturated (WS), water saturated and completely dried (WSD), humid saturated (HS), freeze/thaw (F/T) and water saturated and freeze/thaw (WSF/T) environments: (a) Modulus; (b) Tensile strength.

Fig. 6. The correlation between moisture content (MC) and mechanical properties of Flax/PLA bio-composites: (a) tensile properties, (b) flexural properties.

Fig. 7. The fracture images from the side of the bio-composite after exposure to: a) as-manufactured (AM); b) water saturated (WS); c) water saturated and completely dried (WSD); d) humid saturated (HS); e) freeze/thaw (F/T) 10cycles; and f) water saturated and freeze/thaw (WSF/T) 10cycles and their fracture modes.

Fig. 8. Mechanism for water damage: (a) expansion of a wet fibre, (b) wet composite after molecular relaxation processes, and (c) contraction of the fibre during drying (concept reproduced from <sup>32</sup>).



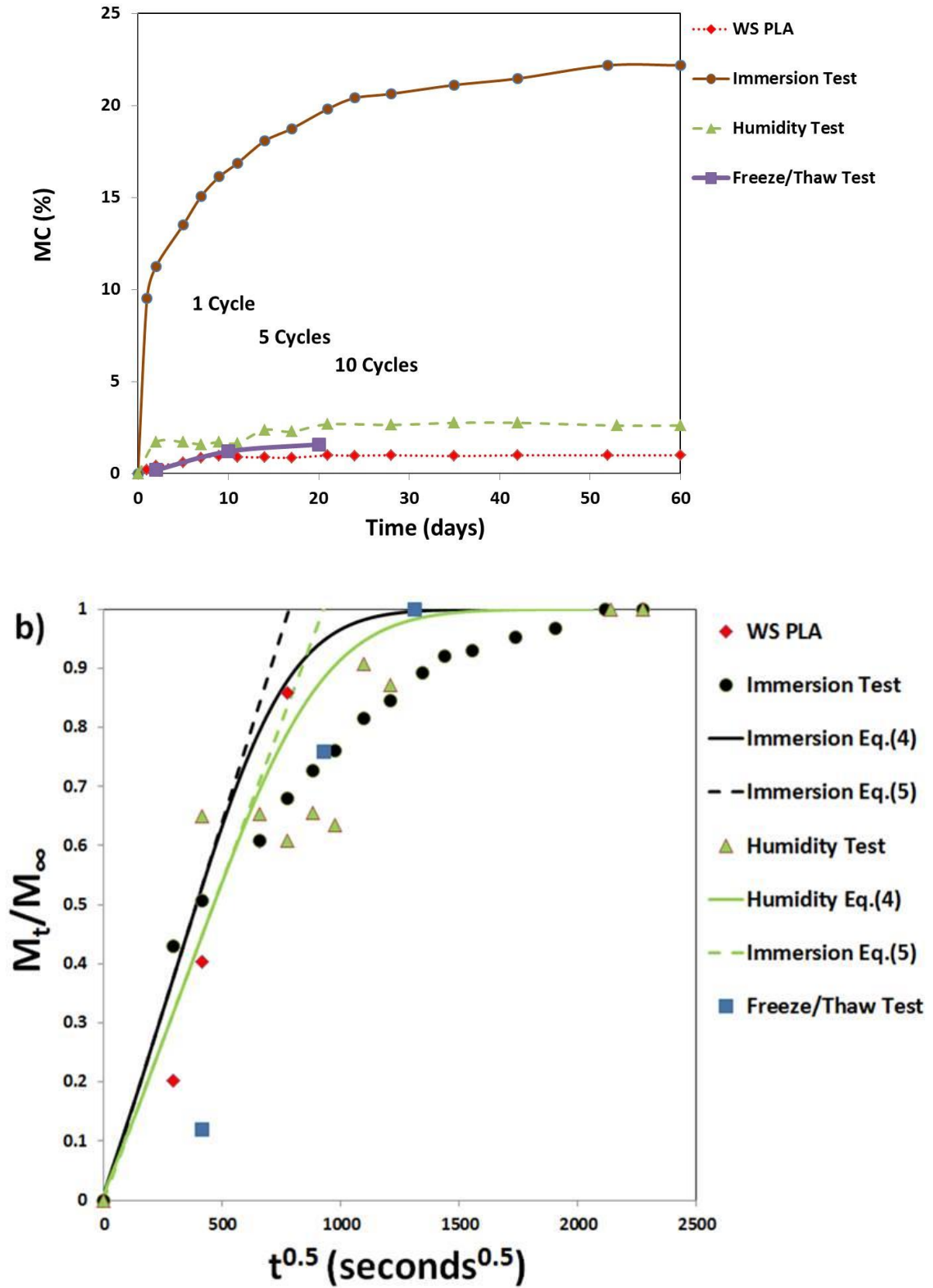


Fig. 1.a) Moisture content (MC) and b)  $M_t/M_\infty$  rates of water saturated (WS) PLA and Flax/PLA bio-composites at WS, humid saturated (HS) and freeze/thaw (F/T) environments.



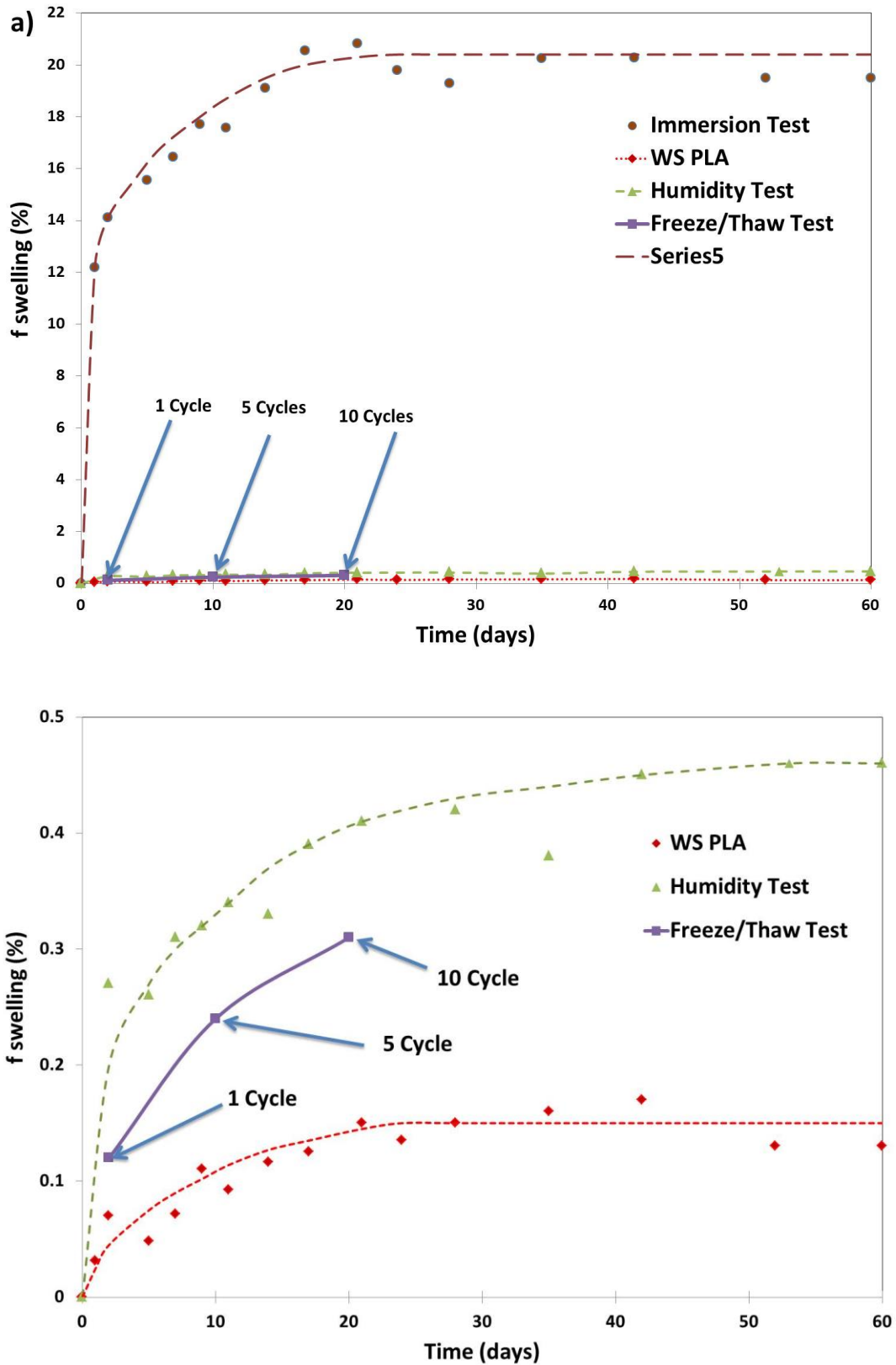


Fig. 2.a) Swelling rate of water saturated (WS) PLA and Flax/PLA bio-composites at WS, humid saturated (HS) and freeze/thaw (F/T) environments; b) magnified swelling rate of WS PLA, bio-composites at HS and F/T environments.

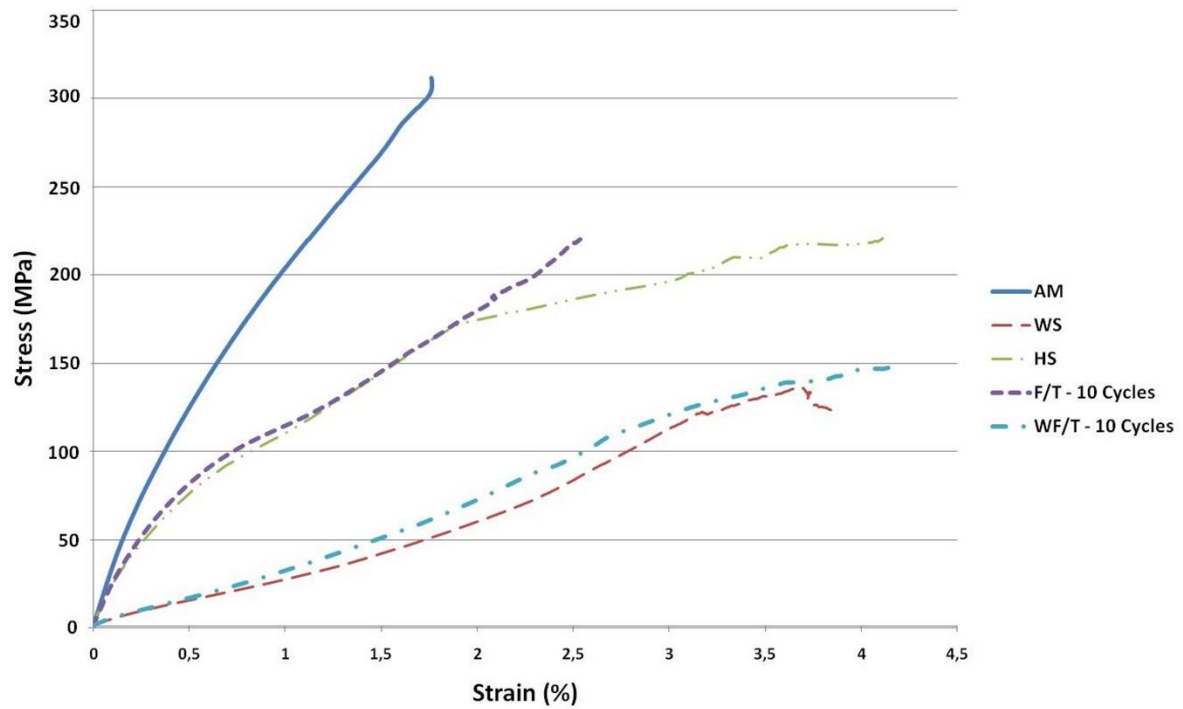


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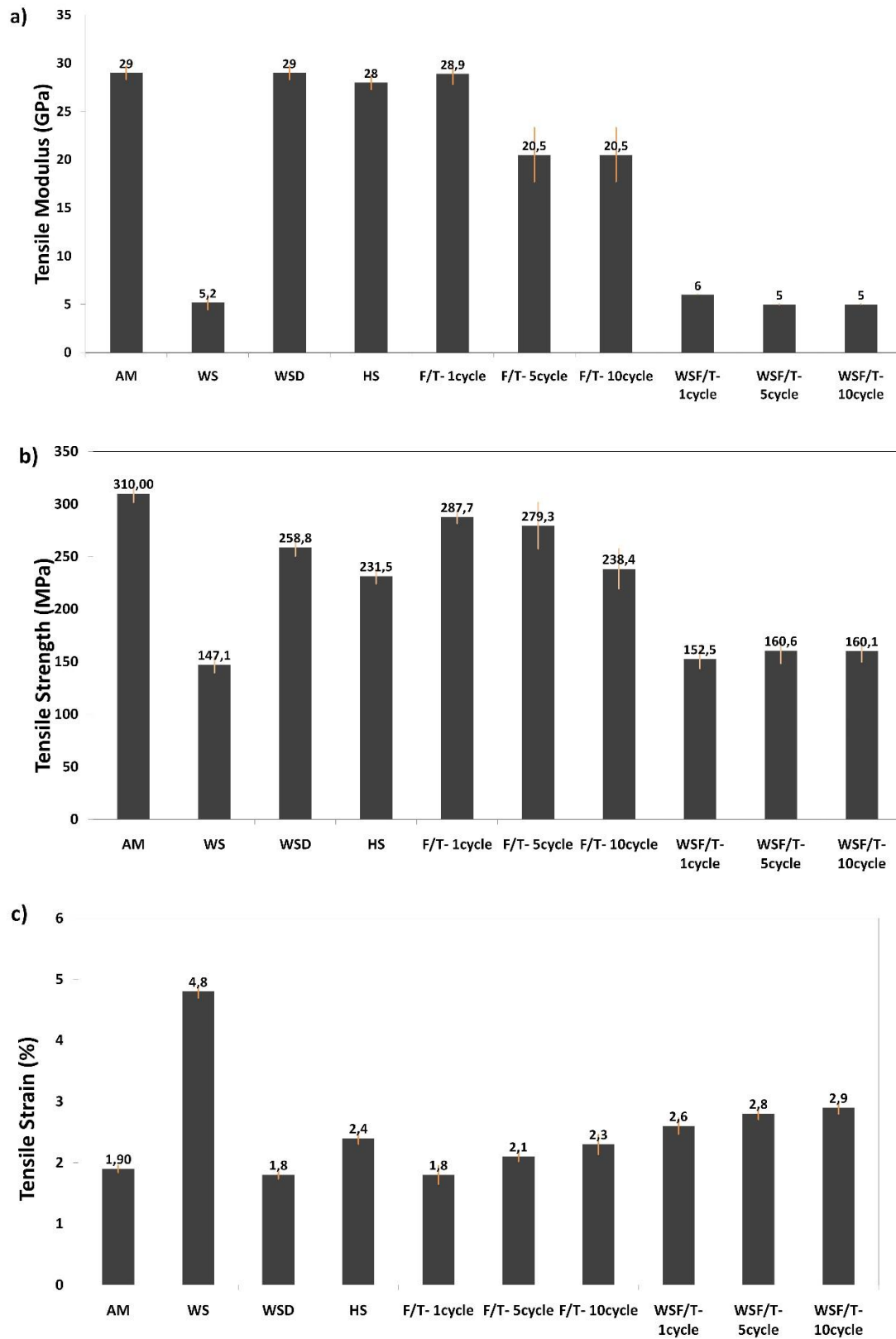


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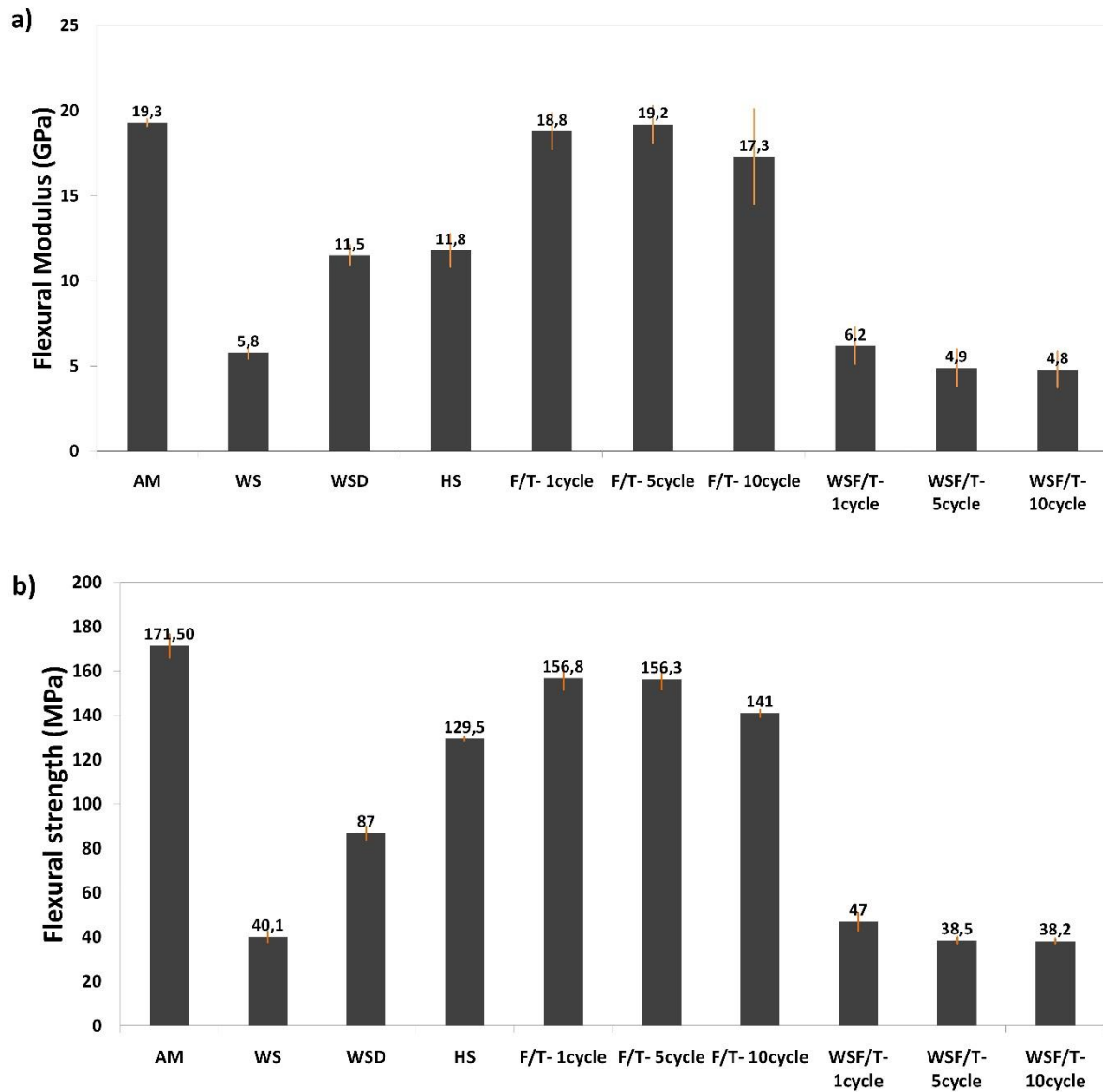


Fig. 5. Flexural properties of the Flax/PLA bio-composite at as-manufactured (AM), water saturated (WS), water saturated and completely dried (WSD), humid saturated (HS), freeze/thaw (F/T) and water saturated and freeze/thaw (WSF/T) environments: (a) Modulus; (b) Tensile strength.

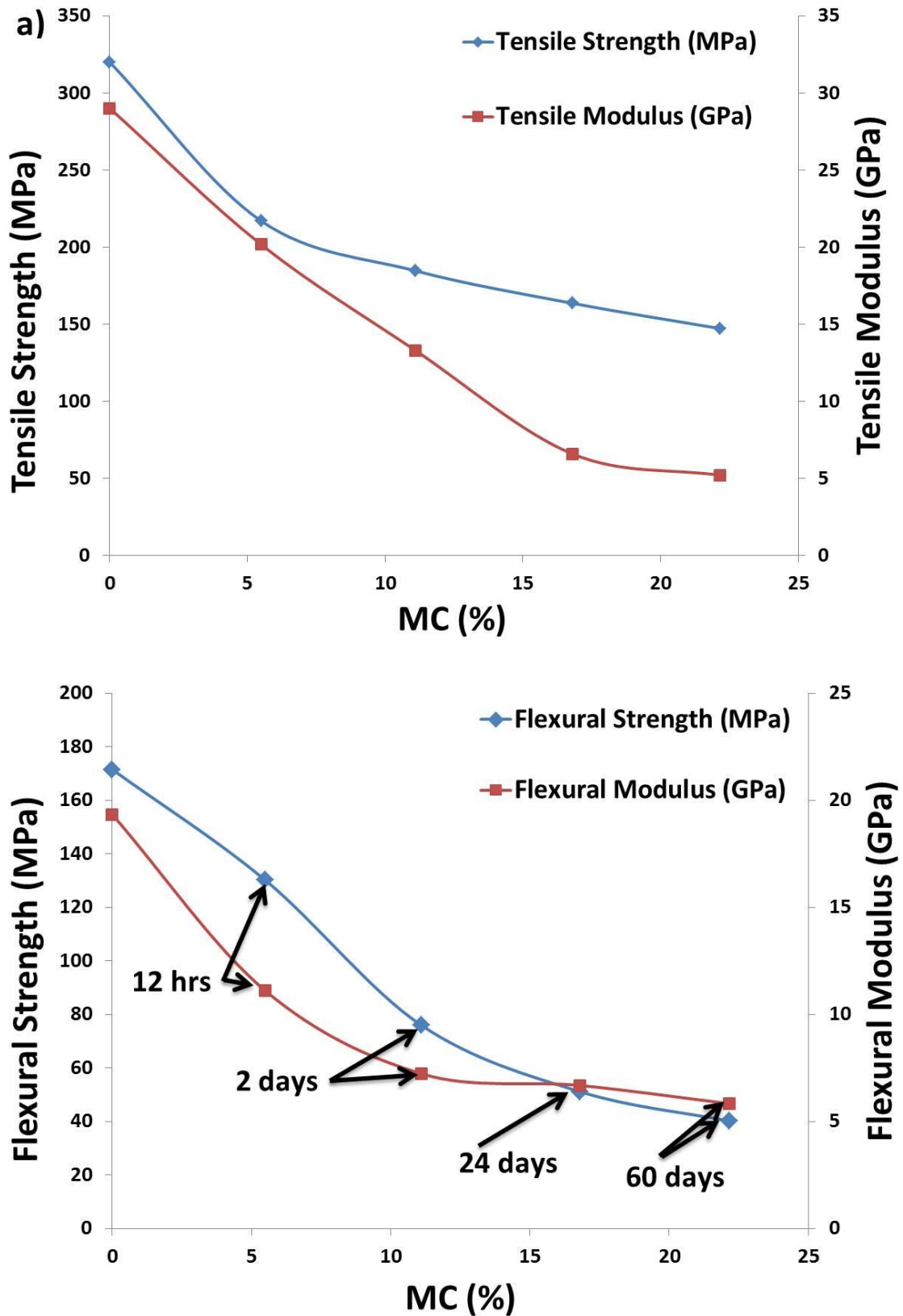


Fig. 6. The correlation between moisture content (MC) and mechanical properties of Flax/PLA bio-composites: (a) tensile properties, (b) flexural properties.

Side view of bio-composites after tensile tests		Tensile fracture mechanisms
<b>a</b>		Fibre breakage or fibre fracture and fibre pull out
<b>b</b>		Matrix cracking and fibre and matrix debonding
<b>c</b>		Fibre breakage, fibre pull out, and fiber and matrix debonding
<b>d</b>		Fibre breakage, and fibre and matrix debonding
<b>e</b>		Fibre breakage, matrix racking, and fibre and matrix debonding
<b>f</b>		Fibre breakage, matrix cracking, fibre pull out, and fibre and matrix debonding

Fig. 7. The fracture images from the side of the bio-composite after exposure to: a) as-manufactured (AM); b) water saturated (WS); c) water saturated and completely dried (WSD); d) humid saturated (HS); e) freeze/thaw (F/T) 10cycles; and f) water saturated and freeze/thaw (WSF/T) 10cycles and their fracture modes.

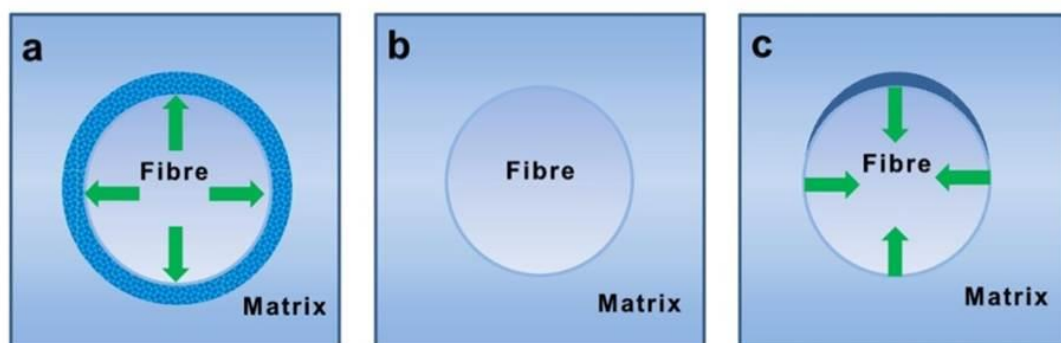


Fig. 8. Mechanism for water damage: (a) expansion of a wet fibre, (b) wet composite after molecular relaxation processes, and (c) contraction of the fibre during drying (concept reproduced from <sup>32</sup>).

Table 1. Previous studies on mechanical properties degradation of NFRP bio-composites using various materials, manufacturing processes and various environments.

Material Fibre/Matrix	Manufacturing detail	Condition	Max. moisture content / Days	Degradation	Ref.
Hemp/ unsaturated polyester	<ul style="list-style-type: none"> <li>Non-woven hemp</li> <li>Method= Hand lay-up compression moulding</li> <li>21% fibre volume</li> </ul>	WS	11% / 6	≈38% decline in tensile strength and ≈97% in tensile modulus	9
Jute/ Bio-epoxy	<ul style="list-style-type: none"> <li>Plain weave jute</li> <li>Method= low-pressure injection moulding</li> <li>40% fibre volume</li> </ul>	WS	26% / 14	High rate of swelling Reduction in density of samples	10
Flax/ polypropylene	<ul style="list-style-type: none"> <li>non-woven needled flax</li> <li>Method= blending in a twin-screw extruder</li> <li>38% fibre volume</li> </ul>	WS	18% / 60	≈25% decline in tensile ≈40% decline in stiffness	12
Jute/ phenolic resin	jute hessian cloth	WS	48%weight gained / 60	≈60% decline in tensile strength ≈60% decline in flexural strength	17
Jute/ PLA	<ul style="list-style-type: none"> <li>Short jute</li> <li>Method= film stacking hot press 40% fibre volume</li> </ul>	HS at 70 °C	16% / 7	≈75% decline in tensile	13
Jute/ phenolic resin	jute hessian cloth	HS at 50 °C	10%weight gained / 60	≈70% decline in tensile strength ≈58% decline in flexural strength	17
Wood Flour/ polyvinyl chloride	<ul style="list-style-type: none"> <li>16-mesh beech wood</li> <li>Method= compression moulding</li> <li>70% weight fraction</li> </ul>	F/T 3 cycles at -18°C	---	30–40% decline in mechanical properties (tensile strength and modulus, and flexural strength and modulus)	18

Table 2. Kinetic Data of water saturated (WS) PLA and Flax/PLA bio-composites at WS, humid saturated (HS) and freeze/thaw (F/T) environments.

FF/PLA composites exposing conditions	Saturation moisture uptake $M_{\infty}$ (%)	Initial slope of plot ( $\Theta$ )( $M_t$ ) versus $t^{0.5}$ ( $s^{-0.5} \times 10^{-3}$ )	Effective Diffusion coefficient, $D$ , $\times 10^{-12}(\text{m}^2/\text{s})$
Neat PLA	0.99	0.4	10
WS	22	28	189
HS	2.60	2.8	136